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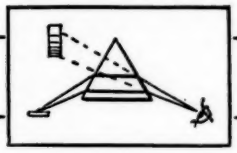

AUGUST
1935



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# The Blackening of Photographic Plates by Long Wavelength X-Rays

F. R. HIRSH, JR., *Cornell University*

(Received May 16, 1935)

The density, exposure-time curves for x-rays of wavelength 4–6A, exhibit an initial region of linearity whose extent increases with the wavelength. At about 6A, the shape of the density, exposure-time curve suggests a tendency towards the familiar shape of the curve for the ultraviolet and visible regions.

## INTRODUCTION

FRIEDERICH AND KOCH[1] first observed that the density exposure-time curve for x-rays is a straight line passing through the origin, but falling below strict proportionality at high densities. Glocker and Traub,[2] using radiation from various fluorescers, observed proportionality up to a density of 0.6. Bouwers,[3] in 1923, observed that the density, exposure-time curve for x-rays falls off linearly in the region of small blackening. Brindley and Spiers[4] exposed successive layers of film to Mo $K$ radiation and observed linearity extending to a density of about 1.5. However, data[5] obtained in this laboratory indicate that the density, exposure-time curve for Mo $K$ radiation, as obtained by a rotating sector disk method, shows linearity only up to about 0.6. Recently, Jauncey and Richardson[6] using W $K$-radiation have observed proportionality extending to a density of 0.6.

All these results, except those of Brindley and Spiers,[4] point to a linearity extending to a density of about 0.6 for the density, exposure-time curve for x-rays of wavelength $\sim$1.0A.

## EXPERIMENTAL

It was of especial interest to determine the extent of the linear region of the density, exposure-time curve for soft x-rays, $\lambda \sim 4.0$ to 6.0A. Sector disk and multiple film methods cannot readily be used in this wavelength region since the radiations are very readily absorbed. Work must be done in vacuum.

The $L\alpha$ lines of Mo, Ru, Rh and Cd were recorded on Eastman IV–0 spectroscopic plates in a Siegbahn vacuum spectrograph. These spectrograms were all made on pieces of the same 4×5 plate, and were developed by the standard development time, temperature curve in a tank of Eastman D–76 fine grain developer. The x-ray tube was operated at 15 kv and 5 ma.

[1] W. Friederich and P. P. Koch, Ann. d. Physik **45**, 399 (1914).

[2] R. Glocker and W. Traub, Physik. Zeits. **22**, 345 (1921).

[3] A. Bouwers, Zeits. f. Physik **14**, 374 (1923).

[4] G. W. Brindley and F. W. Spiers, Phil. Mag. **16**, 686 (1933).

[5] Unpublished results obtained in the laboratory of Professor C. C. Murdock.

[6] G. E. M. Jauncey and H. W. Richardson, J. Opt. Soc. Am. **24**, 125 (1934)



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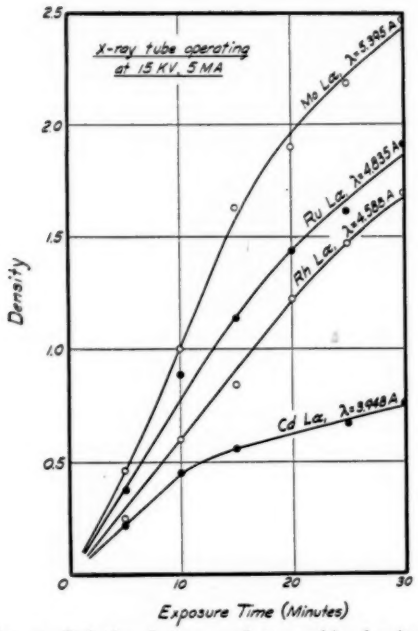


FIG. 1. Relation between photographic density and exposure-time for several x-ray wavelengths, Eastman IV-0 spectroscopic plates.

To reduce errors, a platinum filament coated with oxidized white sealing wax was used as an electron source. This eliminates the absorption due to tungsten deposits on the target, which would have been a source of error, had a heated tungsten filament been used as an electron source.

The density of the maximum of each line was measured with a microphotometer.

## RESULTS

Curves of density plotted against exposure-time are shown in Fig. 1. (Density means the quantity $\log_{10}$ (1/"Transmission").) For the $L\alpha_1$ lines of Mo, Ru and Rh, the linear region is seen to extend beyond a density of 1.0. However for Cd $L\alpha_1$, $\lambda = 3.948$A, the linearity extends only to a density of 0.5. Others, as has been already mentioned[2, 5, 6] in this article, have found that for $\lambda \sim 1.0$A the linear region is of about this extent, (linear to a density of 0.6). This seems to point to a possible error in the results or method of Brindley and Spiers[4] who found linearity extending to a density of about 1.5.

The four-density, exposure-time curves shown in Fig. 1. indicate that the extent of the region of linearity increases with the wavelength. The curve for Mo $L\alpha_1$, the softest radiation used, suggests a possible departure towards the well-known shape of the density-exposure curve found in the ultraviolet and visible regions of the electromagnetic spectrum, since there seems to be a tendency towards a "foot" for this curve.

## ACKNOWLEDGMENTS

The author wishes to express his appreciation of the action of the Cornell Physics Department in extending research privileges. The author especially wishes to thank Professor F. K. Richtmyer for permission to use certain Heckscher Research Council apparatus.

# Light Absorption in the Atmosphere and Its Photochemistry*

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(Received May 25, 1935)

SUNLIGHT, as it penetrates into the earth's atmosphere, is absorbed first at very short wavelengths. The chief molecular constituents of the high air,[1] hydrogen, nitrogen and oxygen, are arranged in the earth's gravitational field in this order with descending height, and absorb, respectively, to longer wavelengths, namely, hydrogen beginning at about 1100A, nitrogen at 1450A and oxygen at 1850A. None of these gases absorb in the infrared or in the visible, except for weak absorption by oxygen. Thus for some distance into the atmosphere the solar radiation probably remains pretty much unaffected to wavelengths longer than 1900A, unless other gases, produced and maintained by photochemical action on these three, show further absorption. Water vapor, while lying principally in the lower altitudes, probably reaches somewhat into the higher ones. It absorbs, however, first below 1800A, and is therefore pretty well blanketed by oxygen, except for what little may get to very great altitudes. The small amount of $CO_2$ in the atmosphere lies close to the earth's surface, and aside from its infrared absorption, absorbs first at 1700A. It is thus of no direct photochemical importance, being blanketed by the gases above. Both $CO_2$ and $H_2O$ absorb strongly in the infrared, of course, but infrared absorption, insofar as it is simple vibration-rotation absorption, produces no photochemical change, only heat. Thus one must look to the gases hydrogen, nitrogen, oxygen and possibly water vapor as the original substances from which other absorbing gases may be produced by photochemical reaction.

The radiation available for this purpose consists of the quanta coming from the sun in the deep ultraviolet, a region inaccessible to direct study. In lieu of direct information we may assume the ultraviolet radiation of the sun to be that given by a Planck curve for 6000°K, which is fairly well approximated out to 3000A. However, deviations from this, such as might occur because of general ultraviolet absorption in the high solar atmosphere or an excess of ultraviolet emission, could affect radically photochemical considerations in the earth's atmosphere. Considering the radiation as black body, however, Fig. 1 gives some idea of how this is distributed. It is a Planck curve for 6000°K but drawn in somewhat unusual units, namely, in quanta instead of ergs, since in photochemical processes it is of course the number of quanta that is of interest. The number of quanta falling on a square centimeter of earth's surface per second per unit frequency band is plotted against frequency. The ordinates correspond to abscissae values in true frequency units (sec.$^{-1}$), but the abscissae are indicated in terms of the more common wave numbers (cm$^{-1}$). In estimating the number of quanta within any frequency interval by means of the area under the curve in this interval, the given ordinates must be used with the true frequency units. The curve conveys little as an illustration other than the fact that the intensity falls away very rapidly in the ultraviolet. Beyond 2000A the rate of decrease is so great that it is represented logarithmically in the upper curve for the rest of the way. The regions absorbed by $H_2$, $N_2$, and $O_2$ are roughly indicated, and of these, accurate and extensive measurements are available only for oxygen.[2] It is chiefly to radiations in these regions that we must look for the photochemical production of new substances. These new substances will be produced over a range of altitudes where the active radiation is absorbed. They may of course be transported also to other altitudes, but it is of primary importance to understand where they are formed.

Because of the approximate exponential distribution of the gases in the atmosphere, the

* Presented by invitation at the Symposium on Atmospheric Optics held under the joint auspices of the American Physical Society and the Optical Society of America February 22, 1935.

[1] Humphreys, *Physics of the Air*, (McGraw-Hill Book Co., New York, 1929).

[2] Ladenburg and Van Voorhis, Phys. Rev. **43**, 315 (1933).

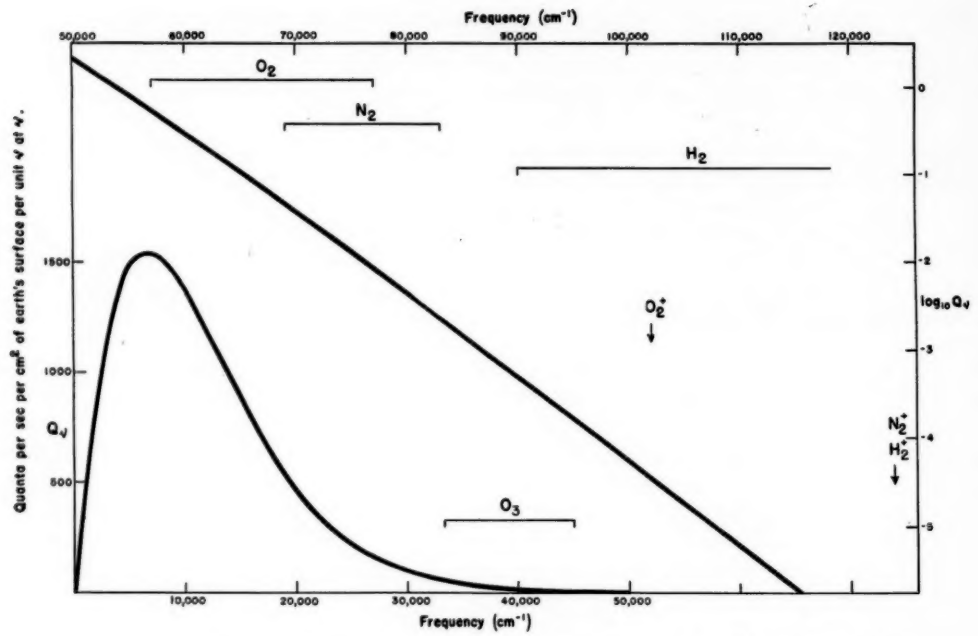


FIG. 1. Distribution of solar radiation at the earth assuming the sun to be a black body at 6000°K.

absorption of radiation of one wavelength is restricted to a relatively narrow region. That possessing a large absorption coefficient will be absorbed at high altitudes. But neighboring wavelengths carrying the same or even greater total energy but of different absorption coefficients will be absorbed at other altitudes, and in particular those having smaller absorption coefficients penetrate deeper and will be absorbed at lower altitudes. For the case of a photochemical steady state, where one set of wavelengths leads to the formation of a new molecule and another set of wavelengths absorbed by this new molecule leads to its destruction, this distribution of absorption is very important.[3]

Where the absorbing gas is distributed exponentially with height, as in a gravitational field, the fraction of the initial intensity absorbed per unit height is the same for all values of the absorption coefficient, except for a transposition in height. Thus Eqs. (1b) and (3a) on page 260 of reference (3) may be written

$$(1/I_{\infty})\cdot(dI/dz)=\alpha\cdot n_0 e^{-pz}e^{-\alpha n_0 e^{-pz}/p},$$

where $n_0e^{-pz}$ (molecules/cc) expresses the distribution in height of the absorbing molecular species and $\alpha$ is the molecular absorption coefficient of the particular frequency of radiation being considered. This is the fraction of the initial intensity which is absorbed per cm of height. It has its maximum[3] at $z_{\max}=-(1/p)\log(p/\alpha n_0)$ and the constant value of $p/e$ at this maximum. The rate of increase in the height of this maximum with $\alpha$ is equal to $1/p\alpha$. Thus the curve of the fraction absorbed per unit height remains the same with changing $\alpha$ except for transposition in height. This fact was overlooked in the argument of reference (3). In Fig. 2, simply as an illustration, three such curves are given, computed for the values of $\alpha$ indicated and a distribution of the absorbing gas $n=1.57\times10^{18}e^{-1.73\times10^{-6}z}$, $z$ being the height in cm measured from $z=0$ at a height above the earth's surface of $1.1\times10^6$ cm, this distribution being practically that for atmospheric oxygen given in Table II, page 70 of reference 1. The area under each curve is, of course, unity. (In Fig. 2 $k$ is used for $\alpha$.)

[3] Wulf, Phil. Mag. (7) **17**, 251 (1934). This article contains a treatment of such photochemical steady states.

The distribution of absorbed radiation may be fairly layer-like, if the curve of the absorption coefficient possesses a rather flat and broad top and has steep sides. But the new molecule formed in a photochemical steady state will not in general be distributed at all like this but will be broadly spread out owing to its formation at many altitudes[3] until new means of decomposition come into play, such as occur at the surface of the earth. Moreover, curves of absorption coefficients usually do not possess broad and flat tops with steep sides, but, rather, rise steadily to a definite maximum and then decrease again. That this is ordinarily to be expected can be seen qualitatively from simple considerations of common molecular potential energy curves and the Franck-Condon principle. What is probably the most important absorption in the atmosphere, that due to oxygen,[2] possesses this latter form of curve.

This distribution of the product is of importance only where absorption takes place in long paths with intensities of the same order of magnitude over a range of wavelengths embracing widely different absorption coefficients. But just these conditions obtain in atmospheres,[3] both stellar and planetary. In the latter case, for the same ratio of absorption coefficients but with decreasing absolute values, the concentration of the new product at its maximum increases, and the height of this maximum falls. The rates of the processes maintaining the steady state will in general vary with altitude, depending upon the curve of the absorption coefficient. For the cases where the producing radiation is completely absorbed and the new molecule concentration is always small compared with that of the original molecule, the total amount of new molecule formed by the two radiations increases with decreasing value of the absorption coefficients. Where, moreover, the absorbing gas is distributed in a gravitational field, such as in the earth's atmosphere, this increase becomes very great. Where the steady state is maintained by very slow processes, we would expect it to be most easily disturbed and to show variations. Furthermore, it is clear from the above that the region of high temperature due to this chemically active absorption is not to be expected where the new molecule is, but where the processes of formation and decomposition proceed at the highest rates, after the heat capacity per unit volume has been duly taken into consideration. This may in general be at high altitudes, quite distinct from the average height of the new substance produced.

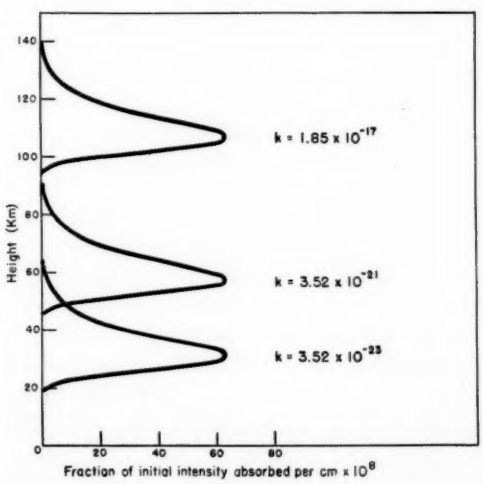


FIG. 2.

At very high altitudes absorption can produce only dissociation, ionization or fluorescence, since there are too few collisons to yield reactions leading to molecule formation. Here also, however, there are some points worthy of note. The characters of the absorptions differ. Oxygen, as contrasted with nitrogen and hydrogen, possesses absorption leading easily to dissociation. This can be seen from the diagrammatic representation of the potential curves of the oxygen and nitrogen molecules given in Fig. 3. The absorptions of interest here are in each case transitions from the lowest curve to the uppermost one. Transitions from the lowest curve to the middle one are very weak in oxygen (giving rise to the so-called "atmospheric bands"), and are as yet unknown in absorption in nitrogen. The chief absorption due to these gases at ordinary temperatures comes from regions of the lower curve in the immediate vicinity of the minimum passing to the uppermost curves on paths spreading only a little on each side of the vertical. Thus in oxygen these transitions are to points on the uppermost curve well above the level of dissociation. Oxygen

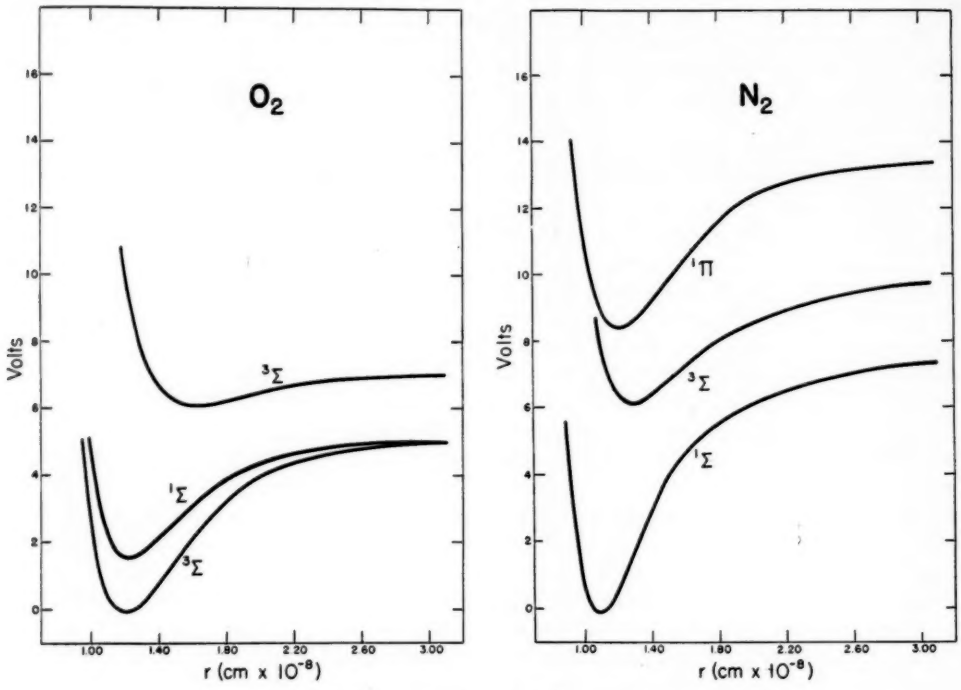


FIG. 3. Diagrammatic potential energy curves.

atoms should be relatively prevalent, therefore, at high altitudes. With nitrogen, dissociation is much less likely, the absorption resulting chiefly in simple excitation. Since hydrogen may not be present in large absolute amounts, and only at very high altitudes, we may consider nitrogen and oxygen alone, though hydrogen is more similar in this respect to nitrogen.

It is interesting that oxygen atoms and nitrogen molecule ions are conspicuous things observed in the light of the night sky and of twilight. The green line and probably the two red lines due to oxygen atoms are prominent radiations observed[4] in the light of the night sky. These are normally forbidden transitions, being $^1S_0$ to $^1D_2$ in the first case and $^1D_2$ to $^3P_{2,1}$ in the second case. However, absorption of sunlight, since they lie in the most intense region of the solar radiation, might account for step-wise excitation of these in large amounts. One might raise the question as to whether it is stretching the lifetime of these metastable states much too far to suggest that they then slowly come back during the night. The mechanism of the emission of the oxygen atom lines in the light of the normal night sky is a matter of much interest. The nitrogen molecule ion radiation is, on the other hand, a permitted transition, a $^2\Sigma$ to $^2\Sigma$ transition, and it is observed in the absence of aurora only when the first or last traces of sunlight touch the high atmosphere.[4] It seems thus that it is a fluorescence phenomenon, due to the absorption of sunlight by the $N_2^+$ ion produced in the high atmosphere photochemically.

Deeper in the atmosphere collisons become frequent enough so that molecule formation can occur in appreciable amounts. The outstanding example is the reaction of ozone formation. This reaction brings into existence the possibility of the opposite photochemical reaction that destroys ozone, because of the absorption of other light by it.[5] Since, in sunlight, there is radiation in

[4] Slipher, Trans. Am. Geophys. Union (1933), page 125.

[5] For the present status of the results on the amount and distribution of atmospheric ozone see Ladenburg, J. Opt. Soc. Am. in press.

both the region of oxygen absorption and ozone absorption, a photochemical steady state is set up.

In this steady state, owing to the importance of weakly absorbed radiations which penetrate to low altitudes, the ozone should be distributed over a wide range of altitudes[3] as has been indicated above. Possibly it is brought to low values at low altitudes only by new methods of decomposition entering, such as chemical reaction with the constituents of the earth's surface. Ozone is a very reactive gas, being presumably rapidly removed by contact with vegetated or populated portions of the earth's surface. It may also be that there exists no appreciable amount of ozone-forming sunlight which possesses an absorption coefficient sufficiently small to penetrate to the surface of the earth.

An important photochemical effect also tending to raise the amount of ozone in low altitudes is the pressure-dependent oxygen absorption.[6] This is something more than weak absorption occurring at low altitudes. This absorption depends upon the square of the oxygen pressure and upon the presence of other gases and hence increases much more rapidly than simply the exponential increase of the oxygen. It, furthermore, leads to ozone formation. There occurs, therefore, a region where considerable amounts of ozone-forming radiation are absorbed at quite low altitudes.[7] The troposphere is a stirred atmosphere and hence this ozone may be observed even at the ground. Furthermore, this low part of the ozone produced by this pressure-dependent absorption, sometimes interpreted as due to the molecule $O_4$, should be dependent upon atmospheric pressure conditions, that is to say, upon weather conditions, as well as possibly upon geographical latitude.

The $O_4$ or pressure-dependent oxygen absorption can account[7] for the failure of all but very small amounts of radiation[8] to get through the 2100–2200A region between the ozone and the main oxygen absorption. It is of interest, however, to inquire what other absorbing substances might also be present. Since small amounts of water vapor presumably reach to high altitudes, the absorption of this substance must be considered. Radiation in the region of 1600–1700A dissociates water into H and OH. There then exists the possibility of hydrogen peroxide. This absorbs continuously across the 2100–2200A region.[9] Existing photochemical evidence indicates, however, in the opinion of the writer, that the photochemical formation of hydrogen peroxide is not apt to occur to any great extent especially at high altitudes.

The results of Götz and Maier-Leibnitz[10] indicate that there is banded absorption in the surface layers beyond the ozone maximum, due to something further than ozone and oxygen. It becomes an important problem to determine what the gas or gases may be that lead to this. They may be of surface origin, but it is perhaps improbable that they are due to artificial origin in the high altitudes of Switzerland. It may be necessary to look for some other photochemically produced atmospheric constituent.

Of the possibilities mentioned earlier an oxide of nitrogen seems most probable. The absorption of nitrogen in the ultraviolet could lead to chemical reactivity with oxygen, though there is as yet no direct experimental demonstration of this photochemical effect. It might be inappreciable at very low pressures. But there is also photo-ionization to be considered as a means of inducing chemical reaction. It seems probable that the absorption which leads to ionization beyond the limit of the molecular electronic levels is not unusually strong, and it would be rather surprising to find it much stronger, or even as strong, as the maximum oxygen absorption at 1450A. In other words, it seems probable that radiation producing photo-ionization penetrates reasonably deeply. An ionized layer can be maintained, of course, only where the pressures are so low as to make recombination very infre-

[6] Salow and Steiner, Nature **134**, 463 (1934); Wulf, Proc. Nat. Acad. Sci. **14**, 609 (1928); J. Am. Chem. Soc. **50**, 2596 (1928). In these papers references will be found to most of the other work on this subject.

[7] Wulf, Phys. Rev. **41**, 375 (1932).

[8] Meyer, Schein and Stoll, Helv. Phys. Acta **7**, 670 (1934).

[9] Urey, Dawsey and Rice, J. Am. Chem. Soc. **51**, 1371 (1929).

[10] Götz and Maier-Leibnitz, Zeits. f. Geophysik **9**, 253 (1933). See also Chalonge and Vassy, J. de phys. et rad. (7) **5**, 309 (1934).

quent. But the ions produced in the deeper altitudes can lead to chemical reaction after the manner studied by Brewer[11] and by Lind[12] with their co-workers. Briefly, one ion leads to the formation of the order of one new molecule in several simple reactions where chain mechanisms do not enter, for instance, of nitric oxide, in the case of a nitrogen-oxygen mixture. This would seem to be also a possible source of nitric oxide, which gas would be fairly stable photochemically at low pressures. At the higher pressures in low altitudes where radiation below 2000A might lead to its decomposition, it is considerably shielded by oxygen. In the presence of oxygen it could be oxidized to nitrogen dioxide and in the presence of ozone to nitrogen pentoxide. The possibility of the existence of such gases, especially ozone and the oxides of nitrogen in the presence of one another, can hardly be judged from laboratory experience because of the entirely different order of concentrations here concerned, and the uncertainty of the conditions of the steady state.

Both nitric oxide and nitrogen dioxide possess banded absorption beyond that of ozone. However, NO and $NO_2$ unite to a small extent to form $N_2O_3$[13] which possesses a strong continuous absorption, covering the region between the oxygen and the ozone absorption. The concentrations of NO and $NO_2$ would be very small and of $N_2O_3$ very much smaller, but, as in the case of ozone, in long paths might be perceptible.

It is interesting that with water vapor this substance $N_2O_3$ causes another new absorption in the near ultraviolet, a group of diffuse bands, due probably to the molecule $HNO_2$.[14] It would be interesting to compare the transparency of the layers near the earth in the ultraviolet 2150A region with the humidity to see if there is any correlation between water vapor and transparency in the 2150A region.

In conclusion it may not be out of place to point out that ozone (and nitric oxide also if present) may conceivably exercise an important biological effect, despite its low concentration. The atmosphere, being constantly stirred against the surface of the earth, probably suffers the rapid removal of such chemically active gases by plant and animal life. That ozone exists at all in the lower atmosphere would seem to indicate that its rate of production in the steady state is relatively high. It may, therefore, be that the rate of supply of such gases makes them biological factors of some consequence despite their low concentration, and this possibility in itself would make desirable an investigation as to their amounts, their variations and their geographical distributions.

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[11] Brewer, *et al*, J. Phys. Chem. Papers I to XIV on *Chemical Action in the Glow Discharge*. From 1929 to date.

[12] Lind, *Chemical Effects of Alpha Particles and Electrons* (Chemical Catalog Co., New York, 1928).

[13] Melvin and Wulf, Phys. Rev. **45**, 751 (1934).

[14] Results obtained by Dr. Melvin and the writer, now being prepared for publication. These indicate that the banded portion of the above spectrum is due to a complex involving $N_2O_3$ and $H_2O$, not to $N_2O_3$ alone as originally believed.

# Visibility of Signals Through Fog*

GJON MILI, *Westinghouse Lamp Company*

(Received May 25, 1935)

Light does not penetrate far in a very dense fog, and the problem of safe navigation through fog cannot be entirely solved by the use of light signals. In harbor, canal and river navigation it is common practice to indicate the course by means of signal lights so placed as to provide clear visibility and directional guidance in fair weather. The usefulness of such systems of signal lights can readily be extended to include less favorable weather conditions, such as mist, rain, snow and even fog of appreciable density, by proper spacing and design of the units to insure high efficiency and proper light distribution within the angle of view. The principle of varying the lamp voltage to reduce or increase the beam intensity in accordance with weather conditions is suggested.

IT is common experience that in most signal lighting systems the range of vision in fair weather is much greater than is necessary for safe navigation. This is of course true because a fairly clear atmosphere causes no appreciable reduction in intensity, and even lights of comparatively low candlepower may at times be seen for miles. However, with only a very slight degree of turbidity in the atmosphere, such as may occur during mist or light fog, the initial intensity of the beam is cut down at an exponential rate and signal visibility becomes very uncertain.

## VISIBILITY OF SIGNALS

The question as to what constitutes visibility of a signal must be considered. The sensitivity of the eye is highest when it is fully adapted to perfect darkness. For a point source of light only the central or foveal region of the retina is stimulated. Reeves[1] finds that under these circumstances a source of light having an intensity of $2\times10^{-8}$ candle is just perceptible at a distance of 3 meters. In other words, were it not for atmospheric absorption one candle should be visible at a distance of 13 miles. This figure indicates a much higher degree of eye sensitivity than the values established at long range in a clear atmosphere. Experiments carried out by the Deutsche Seewarte[2] and independently by Paterson and Dudding[3] give the practical limit of visibility of lights at sea as approximately 0.35 and 0.31 candle at a range of one mile. Paterson and Dudding also give the more frequently used figure of 0.12 kilometer-candle as the practical limit of threshold visibility.

## THE EFFECT OF FOG

The effect of fog on the visibility of the signal light is twofold: First, it reduces the apparent candlepower of the beam through diffusion; and, second, it creates a background of light which reduces the brightness contrast between the signal light and its immediate surroundings.

The degree of opacity of a foggy atmosphere to direct light depends on the size and concentration of the drops. Knowing the transmission of a given thickness of atmosphere, the reduction in candlepower may be computed on the basis of the following equation:

$$E_t = I_0 \times t^D / D^2,$$

where $E_t$ = the illumination at the point of observation, $I_0$ = initial candlepower intensity; $t$ = transmission coefficient per unit length of turbid atmosphere; $D$ = distance between the signal and the observation point.

The attenuation of the emergent light intensity, however, is far less important than the diffusion effect which, by reducing the contrast between the light source and its background, increases the threshold intensity required for visibility. In a night fog the background may be considered as adding little if any illumination to reduce the brightness contrast, and the circle of light around the source is created entirely by the diffusion of the emergent beam. During daylight, however, the brightness contrast between a signal

* Presented by invitation before the Optical Society of America at its session on Atmospheric Optics, February 22, 1935.

[1] Reeves, Astrophys. J. **47**, 141 (1918).

[2] Deutsche Seewarte, Eng. News **33**, (1895).

[3] Paterson and Dudding, Proc. Phys. Soc. **24**, 379 (1912).

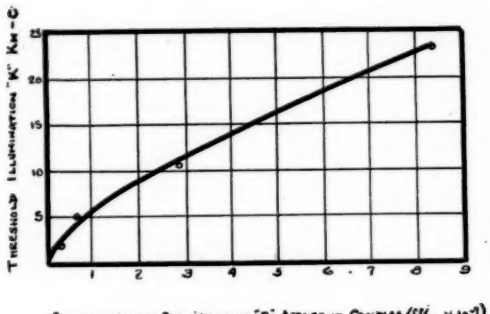


FIG. 1. Relationship between illumination required for threshold visibility of a point source of light and background brightness.

and its immediate surroundings is further decreased by the diffuse illumination provided by the sun and the sky. Obviously, since the visibility of a signal depends primarily on the contrast it offers with its background, fogs offer a more serious problem in daylight than at night. Bennett[4] states that the visual range during a day fog is approximately half that during a night fog of a similar character. Bennett has studied the problem of the increasing threshold value required for visibility of a point source of light with increased background brightness, and his results are embodied in the curve shown in Fig. 1. The values obtained follow closely the equation:

$$K = 0.12 + 10^{-4} B^{2/3},$$

where $K$ = illumination for threshold visibility in kilometer-candles, and $B$ = background brightness in apparent candles per kilometer². The value of 0.12 in the second member of the equation represents the illumination required for threshold visibility with zero background brightness, which was obtained experimentally.[5] The full equation for threshold visibility during fog now becomes:

$$I_0 \times t^D / D^2 = 0.12 + 10^{-4} B^{2/3}.$$

It appears from this equation that it would be possible to determine the candlepower required for a light to be visible at a definite distance during fog if the coefficient of transmission and the background brightness were known.

[4] Bennett, Roy. Meteor. Soc. J. **58**, 259 (1932).

## Optical Characteristics of Signal Units

The optical characteristics of a signal light may be considered to be:

(a) brightness
(b) size
(c) candlepower distribution
(d) color

It has been found that at very low intensities visibility depends mainly on the candlepower and very little on either actual brightness or size alone, as long as the light source subtends an angle of less than 50′ at the eye.[5] This means, as Walsh points out,[6] that at very low intensities the psychological effect of light is cumulative and independent of the area over which it is distributed. Since in signal work we are dealing with almost point sources of light, and in fog very low intensities prevail, it is safe to assume that the above statement will hold very closely.

The candlepower distribution is significant where more than one unit at a time is required to establish the course of navigation. The ideal distribution is that which offers equally good visibility within the angle of vision of the observer.

While various investigators have pointed out that fog has a slight color selectivity, most lights appearing slightly more yellow when viewed through fog than when viewed through a clear atmosphere, the effect is not very significant and may be neglected. The point has often been raised that colored signals present an appearance distinctly different from any surrounding lights and are therefore more readily recognizable. This is of course true, although, according to Breckenridge and Nolan,[7] screening off a portion of the visible spectrum of a signal light with a corresponding reduction in beam candlepower has not been found advantageous to visibility.

## Fog Data Available

A survey of the literature has yielded only one source giving definite information for day fog conditions as to the increase in visual range of

[5] S. D. Chalmers, Opt. Soc. Trans. **20**, 297 (1919).
[6] J. W. T. Walsh, *Photometry*, Chap. III (1926).
[7] Breckenridge and Nolan, Bur. Standards J. Research **3**, 11, Research Paper No. 78 (1929).

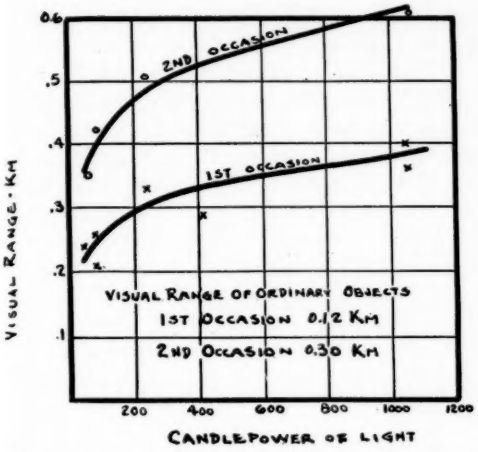


FIG. 2. Experimental observations of the visual range of light sources of various candlepower intensities during day fog.

a signal with increase in candlepower.[8] The curves in Fig. 2 show the increase in visual range for two different day fogs with increase in candlepower from 50 to 1000. During one fog the ground was visible up to 0.12 kilometer, during the other up to 0.30 kilometer. It may be seen that in the denser fog the visual range of a light of 50 candlepower was double that of objects, and that if the candlepower is raised to 1000 the visual range is three times that of objects. After solving for the transmission coefficient it may be deduced from the formula that a 500,000-candlepower signal would have a visual range about six times ground visibility, or three times that of a 50-candlepower lamp.

## THE SIGNAL UNIT

The lamps used for signal work may vary from only a few candlepower in the case of low voltage miniature lamps to as high as 1000 candlepower in the case of street series lamps. Bare lamps are essentially converters of electrical energy into light, and they radiate light almost evenly in all directions, whereas in most signal work the effective angle of view is very limited. This is shown in Fig. 3, where is depicted a theoretical installation requiring four lights for proper visibility with the observing point at a distance from the shore equal to the spacing between units. In clear weather the intensity of the light farthest from the point of observation need be only ten times the intensity of the nearest light, directly opposite the point of observation. In foggy weather, however, the relationship is decidedly changed. Assuming a fog such that only one-tenth of the light from the nearest source is transmitted, the intensity of the most distant light should be about 200,000 times that of the nearest one. The candlepower distribution which would insure equal visibility of the four signal units in clear weather and in fog of this character is shown in Fig. 4.

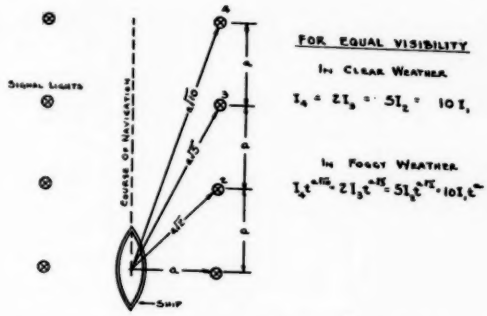


FIG. 3. Hypothetical installation of signal lights to illustrate candlepower requirements for equal visibility from various angles of view.

It is evident that for the situation shown in Fig. 3 the candlepower distribution requirements for fog are entirely different from those for clear weather. In the former case a highly concentrated beam of light of narrow divergence and exceedingly high candlepower is required, whereas in the

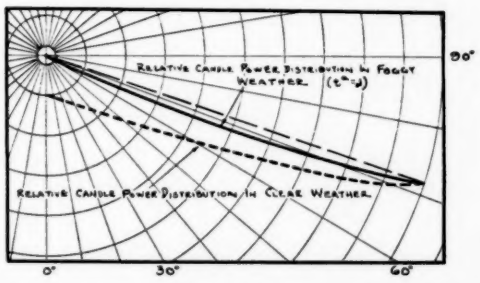


FIG. 4. Relative candlepower distribution in clear and foggy weather for the hypothetical installation shown in Fig. 3.

[8] W. H. Biggs, Meteorol. Mag. **65**, Dec. (1930).

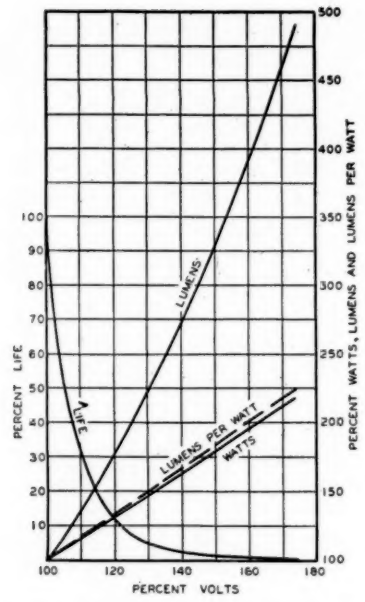


FIG. 5. Characteristic curves of Mazda lamps. Life, light output and efficiency performance for over-voltage operation of lamps.

latter low candlepower such as provided even by bare lamps is sometimes sufficient. A signal unit designed for fog penetration obviously demands the use of a highly concentrating optical element such as a lens or a parabolic reflector.

A further possible step to increase beam intensity is over-voltage operation of the lamp. The relationship between lamp life, light output and over-voltage is indicated in Fig. 5. Reducing the life of the lamp to ten percent will almost double its light output, while reducing it still further to one percent will increase its light output almost four times. This practice is merely suggested for conditions of extremely poor visibility, the maintenance of an economical lamp life being obtained by operating lamps at a correspondingly lower voltage during periods of good visibility.

## SUMMARY

As indicated by this study, three steps are involved in a practical solution of the fog signal problem:

(a) The location of signal lights as close together as is convenient and consistent with installation and operating costs.
(b) The design of a signal unit to provide maximum visibility throughout the angle of view by means of lenses or reflectors.
(c) The variation of candlepower intensities, depending on weather conditions, by varying the operating voltage of the lamps.

# Prism Spectrographs with Prism Mountings Automatically Adjusted to Minimum Deviation

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(Received April 20, 1935)

THE prism spectrograph has long been used as an instrument for observing and photographing spectra. The practical application of prism instruments to so many problems in the various sciences makes them standard equipment in every laboratory. Until a few years ago it was common practice to use one prism as a dispersion piece, a 30° glass or quartz prism silvered on the back surface for a Littrow spectrograph and a 60° prism for the ordinary spectrograph. With the recent development by Twyman and Green[1] of an interferometer method for the correction of prisms for inhomogeneities in the glass or quartz two or more prisms may now be used with a considerable increase in the resolving power of the instrument. Previously when several prisms were used in tandem the angular dispersion was increased proportionately but the resolving power, due to inhomogeneities, was not increased.

With corrected prisms now available the problem arises as to the adjustment of two or more prisms for minimum deviation. This is a particularly important problem in the case of (Cornu) quartz prisms for the reason that the light must travel as nearly as possible along the optic axis to prevent doubling of the lines due to double refraction. For ultraviolet light a single prism is readily set at a given wavelength and at minimum deviation by the use of divided circles. When two or more prisms are used however, it is customary to calculate the angles for the prisms or to use one of the many automatic arrangements developed by Wadsworth, Young and others.[2]

A schematic diagram of a two-prism Littrow spectrograph is shown in Fig. 1. The two prisms are shown in two different positions to show that the second prism must not only rotate through three times the angle of the first prism but must also move as a whole to a new position if the whole aperture is to be used. This is necessary to obtain the maximum resolving power.

The mechanical arrangement that has been devised to do this by one single adjustment is shown in Fig. 2. The lens $L$ and the bed plate $A$ carrying the prisms $P_1$ and $P_2$ are shown mounted together so that the system as a whole moves on the ways $W$ when focusing the instrument. It is not necessary to have the prisms move along with the lens. They may be mounted separately and remain at rest since the light entering and leaving the prisms is parallel.

The base plate $B$ on which the first prism $P_1$ is mounted pivots about $C_1$ and is rotated by means of the worm and gear $WG$, and knob $F$. Prism $P_2$ is also carried around by this plate but is free to turn about the pivot $C_2$. The rotation of the plate which carries $P_2$ by the correct amount is brought about by the steel tape $T$. One end of this tape is partially wrapped around and fastened to the circular arc $V_2$, $V_2$ being screwed to the bed plate $A$. The other end of the tape is partially wrapped around and fastened to the disk $V_1$. $V_1$ is fastened to plate $E$ carrying the second prism. This tape is held under tension by means of another steel tape $T_2$ and spring $S$. Steel tape $T$ is adjusted to the proper length by the screw $O$. The small block $M$ to which the tape is fastened slides on two pegs $Q$ and is moved by the screw $O$. The distance between the two centers $C_1$ and $C_2$ should be equal to or slightly greater than the largest 60° prism

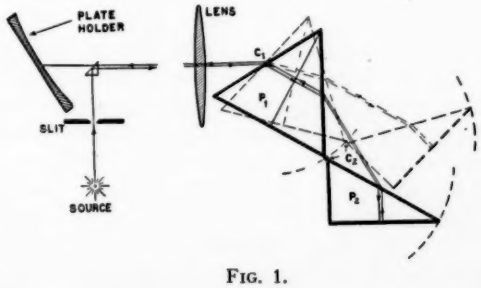


FIG. 1.

[1] See, Twyman, Phil. Mag. **35**, 49 (1918).

[2] For an account of the various methods previously developed see Wien-Harms, *Handbuch der Experimentalphysik*, Vol. 21, 1927, pp. 226–250.

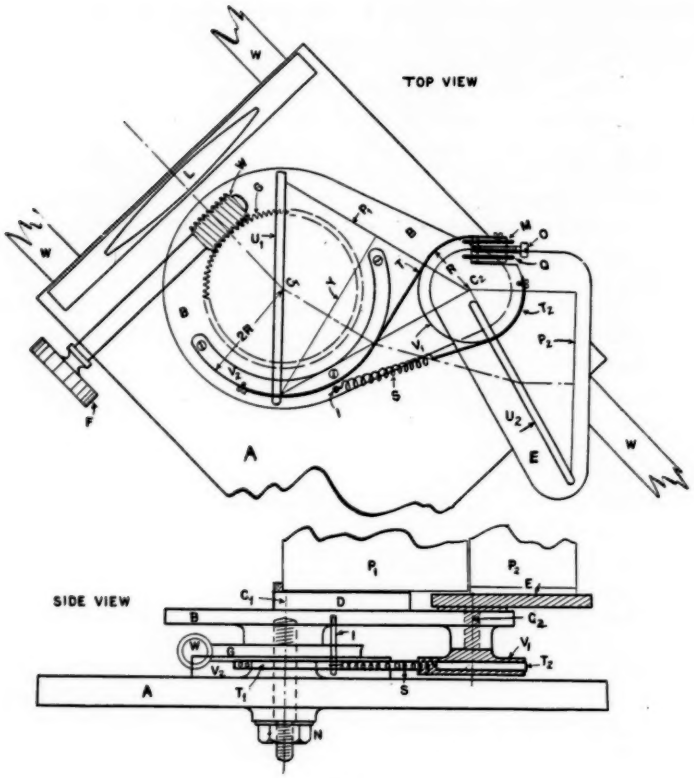


FIG. 2.

to be used in the instrument. If smaller prisms are to be used the front face of the first 60° prism is centered at $C_1$ and the second 30° prism moved along the guide $U_2$ until it too is centered in the beam. The two prisms need not be the same size for the proper operation of the instrument. It is important to note that the radii of the circles $V_2$ and $V_1$ have the exact ratio 2 : 1.

The prisms are adjusted once and for all by the following method. When light is incident upon the prisms a faint spectrum with one-third the dispersion of the regular spectrum will be seen superimposed upon the regular spectrum. This is due to the partial reflection of light at the prism surface in the center of the 60° Cornu prism. The light is reflected back at this surface to give the ghost spectrum. Any given line of this spectrum is set at the center of the plate holder by rotating the 60° prism by the knob *F*. The second prism is now rotated by means of the screw *O* until the same line in the regular spectrum is at the center of the plate holder and superimposed on its ghost line. When this is done the prisms are exactly at minimum deviation for the spectrum line chosen. If now the knob *F* is turned, each of the various spectrum lines of the regular spectrum will be seen to cross the center of the plate holder at exactly the same instant as the corresponding ghost line. An angle calibration of the plate *B* now enables the rotation of the prisms into the ultraviolet region to any wavelength with the assurance that the prisms are at minimum deviation.

A convenient device for eliminating the ghost spectrum (and this must be done) is to bring the regular spectrum to focus through a narrow horizontal strip opening in front of the plate

holder. The ghost spectrum is then thrown just above this opening by tilting the first prism slightly

If glass prisms are used there will be no ghost spectrum, in which case the 30° prism is first placed on the first prism table and a given spectrum line brought to the center of the plate holder by the knob *F*. The two prisms are then mounted in their proper place as in Fig. 2 and the same line again brought to the center by the screw *O*.

If only a 30° prism is to be used in the instrument it is placed on the plate *B* in place of the 60° prism and no adjustments are necessary for minimum deviation.

The above-described apparatus may be applied to a spectrograph containing two Cornu prisms set up as shown in Fig. 3. It is obvious that for this type of instrument the mechanism is the same as that shown in Fig. 2. One addition proves to be convenient, however, and that is a direction-indicator at the third pivot point $C_3$ to give the direction of the outgoing light. This indicator may consist of a small lens, slit and flash light bulb on a small arm pivoted at $C_3$. This optical arm is rotated by two additional disks and steel tapes as described above for Fig. 2. These disks have the same radius; one is centered at $C_2$ and is fastened to the plate carrying the first prism (*B* in Fig. 2.) and the other pivots at $C_3$ and rotates in plate *E* Fig. 2. The optical arm is carried by the latter disk.

Because of the complicated motion of the second prism the camera lens and plate holder are mounted on a single beam which pivots at a fixed point $C_4$. This point must be determined

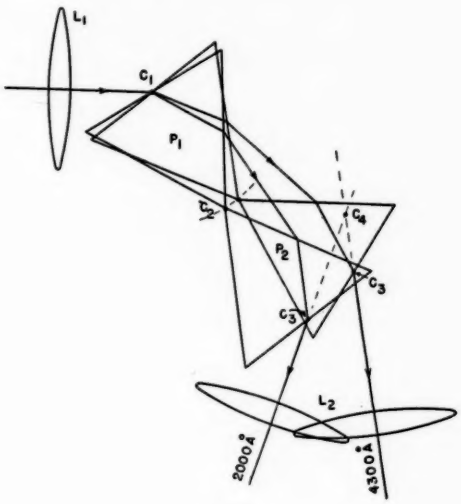


FIG. 3.

for each spectrograph for its position depends upon the size of the prisms and the angular range through which the prisms will be used. Fig. 3 is drawn for two Cornu prisms in the two limiting cases for which they are used, 2000A to 4300A.

In the three-meter quartz spectrograph built in this laboratory the slit is fixed on one concrete pier and the parts shown in Fig. 3 are on another pier. The camera lens and plate holder are mounted together on an eleven-foot iron *I* beam pivoted at $C_4$, a steel center in the concrete pier. Focusing is accomplished by adjusting the lens $L_1$ and $L_2$. The space $L_1$ to $C_1$ is about 18 inches to provide space for Fabry-Perot etalons, echelons or Lummer plates.

# A New Microdensitometer Based on That of Hartmann

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(Received May 23, 1935)

PROBABLY the best known and most widely used of microphotometers for the photographic determination of the intensity of spectrum lines is that devised some 35 years ago by Hartmann for the measurement of star magnitudes.[1] Because of the considerable accuracy obtainable with this instrument and its relatively low cost it is likely that this form of microphotometer will continue to retain its popularity.

The present design aims to retain the essential features of the original form while still further simplifying the construction. This is made possible partly because of the restriction of its application to the measurement of spectrum lines.

The principal feature of the Hartmann design consists in the utilization of a divided beam from a milk glass, one beam serving to illuminate the photographic plate, which is situated on a horizontal table, the other serving to illuminate the wedge. The latter in the original Hartmann instrument was a photographic plate varying in density from one end to the other, but in an arbitrary way. The plate and the wedge were in the original instrument projected by similar microscope objectives onto a Lummer Brodhun cube having the form of a small (apparently) circular reflecting spot in the center, and this is viewed by a horizontal eyepiece.

Because of the small area of the plate observed in measurement a special means of finding had to be employed, and for this Hartmann arranged the cube to slide sideways and give place to a reflecting prism with reference mark in accurate registration with the reflecting spot on the cube. An awkward feature of this method is that the plate has to be adjusted by the help of a perverted image: forward and back motions of the plate are uninverted, but left and right motions are inverted. For this reason the Hartmann design of ocular was modified by the Gaertner Scientific Corporation some years ago, the base plate being turned up to an angle of about 45° with the horizontal, the plate supported by a *T*-square, and the ocular placed directly facing the plate. The cube then has a dividing surface the inverse of that of Hartmann—an unsilvered apparently circular area in a full silvered surface. This modification is carried over in principle to the present design.

The device which the Hartmann instrument employs for finding, the sliding cube, must be nicely made and is an item of some expense in the construction, besides requiring an extra operation in its use. The use of a photographic wedge, while not without attractive features, has some rather serious drawbacks. Local variations of the density in the wedge are apt to result in abnormal local gradients, and identifiable clusters of silver grains can easily result in bias in making a series of settings. Moreover one has to have several wedges for various sizes of grain—a circumstance which has led some workers to prefer to defocus both wedge and plate to eliminate grain as far as possible.

The practice of defocusing to eliminate grain has, however, serious disadvantages. Dust specks and dust lines, and isolated abnormal grain or clusters of grain will be broadened out by such means and will affect the density reading, while, if seen in focus and identified, they will usually

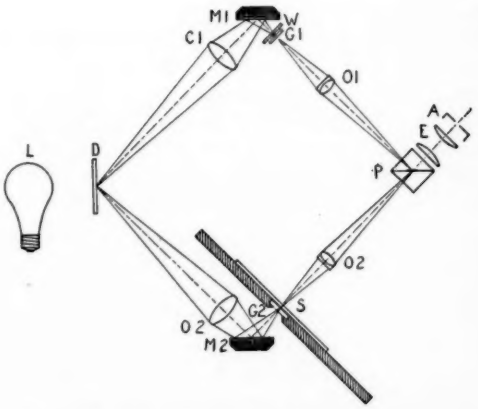


FIG. 1. Optical diagram of new microdensitometer.

[1] J. Hartmann, Zeits. f. Instrumentenk. **19**, 97 (1899).

[[FIG. 2. Field unmatched. FIG. 3. Field matched.

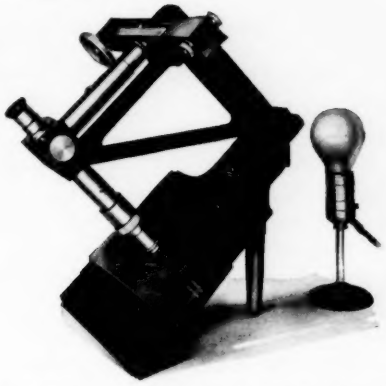

FIG. 4. External appearance of microdensitometer.

not affect the match. Defocusing also is objectionable in that it gives a complicated average of the density over the width of the line. Most of these objections, though not the last, apply to suggested devices for astigmatizing the image.

In the new construction we have sought to avoid these difficulties by keeping the spectrum plate in focus as did Hartmann, while using a neutral dyed gelatin wedge for which the law of increase of density is linear. For this reason we have called the present instrument a microdensitometer. The neutral dyed gelatin wedge made by Eastman Kodak Company (*W* Fig. 1) has a length of 10 cm, its density varying from 0 to 4.0. This carries an index which reads against a millimeter scale, the wedge being mounted on a steel tape which is stretched over two pulleys, one of them with knurled head.

To match accurately the grainless wedge with the grained spectrum plate is not easy. This difficulty is overcome by utilizing a grained plate *G*1 Fig. 1 (of density about 0.5) in the object plane of the comparison microscope. A compensating plate *G*2, cut from the same piece is placed below the stage *S* to preserve the balance. Such grain plates are readily made by the user from any type plate by fogging and developing, and are readily interchanged in the instrument.

The optical arrangement is shown in Fig. 1.

The sliding cube of Hartmann is dispensed with. Instead a horizontal silvered strip covering 0.8 mm of the plate is employed in the cube, this serving to reflect the field of the wedge and its grain plate. The center of this strip is traversed by a slit 0.1 mm wide permitting one to see through it the image of the center of the field on the spectrum plate. One thus sees the field which covers 5.5 mm of the plate as in Fig. 2, the ends of the spectrum lines projecting beyond the strip on top and bottom, the central 0.8 mm of the spectrum line being seen as well if it is in the center of the field. In adjusting the plate it is therefore only necessary to bring the line to be measured, which is at all times in view, onto the slit. The wedge is then adjusted until the density of the wedge as seen in the horizontal strip matches the density of the line as seen in the vertical slit. The appearance of the field when so matched is seen in Fig. 3. The external appearance of the instrument is seen in Fig. 4.

To facilitate adjustment of the plate, the *T*-square support is racked up and down by a pinion at the right of the instrument, and the plate is shifted left and right by a rubber friction roller (not shown in Fig. 4), situated at the center of the *T*-square.

Tests show that the introduction of the grain plate reduces the inaccuracy of setting by about half, the mean deviation from the mean being about ½ percent of the density. The grain in the comparison field results in a noticeable increase in comfort, particularly when the plate being measured has a slight tint.

We believe that the simple operation and the accuracy obtainable should make this instrument a very useful accessory for spectrophotometry and for quantitative analysis with the spectrograph.

It has been applied to the study of x-ray diffraction patterns produced by cellulose fiber.[2]

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[2] Sisson and Clark, Ind. Eng. Chem., Analyt. Ed., 5 296 (1933).

# The Fading of the Latent Photographic Image on Standing

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(Received April 17, 1935)

## INTRODUCTION

IT has long been known that there is generally a change in the latent photographic image during the interval between exposure and development. Recently studies have been made by several investigators as to how this effect is modified by the presence of various desensitizers. The various investigators, however, do not seem to agree, some claiming a growth of the latent image and others a decrease, with the majority inclining to the latter.

In his *Encyclopaedia of Photography*, 1896, Woodbury wrote, under the heading of *Continuing Action of Light:* "It has however been established that no measurable modification takes place in the latent image between exposure to light and development, and that an under-exposed image is under-exposed in the same proportion if the development is deferred some weeks."

Brush[1] finds a growth of the latent image after exposure "which probably reaches its maximum in 15 to 20 minutes," followed by a relapse "which probably begins within an hour or two after exposure."

Weinland,[2] however, in his paper on intermittency says: "In no case was anything observed which could be attributed to such an effect as that described by Brush."

Caroll[3] concludes that "The loss of density on keeping, with active desensitizers and fine-grained plates, is very considerable."

Mauz[4] concludes that "the tendency for reversal is a more or less dormant property of the emulsion which is awakened or strengthened by the dye."

Narbutt[5] repeating the work of Mauz,[4] and verifying the latter's conclusions, found a distinct decrease in the latent image on standing, and that the effect was accentuated in plates desensitized with pinacryptol yellow.

Bullock[6] has made an extensive study of the "spontaneous growth" of the latent image after exposure. He concludes that there is a strong presumption in favor of the logarithmic relation of Jausseran[7] and in favor of an intensification which is already going on before the exposure is terminated and probably at the same speed as in darkness. His results indicate that the period of delay of development should be measured from the middle rather than from the end of the exposure.

## DISCUSSION

Blair and Leighton[8] have suggested an equation for the rate of formation of the latent image which is based upon the hypothesis that the developable latent image is the result of two simultaneous reactions taking place within the emulsion, (1) a forward reaction tending to make the silver halide grains developable, and (2) a reverse reaction tending to return the developable grains to the undevelopable state. In a recent paper on the effect of intermittency[9] the authors suggested the probability that these reactions do not cease immediately upon the termination of the exposure but exhibit a certain inertia or photochemical lag. This assumption of a photochemical lag has been substantiated by the work of Zimmerman,[10] although he claims not to have detected the Brush[1] effect.

On the basis of the assumptions of Blair and Leighton[8] and of the authors[9] the apparent contradictions in the reports of the various investigators cited above can easily be harmonized. If at the termination of an exposure the forward reaction has attained a relatively high

[1] Brush, Phys. Rev. **31**, 241 (1910); Brit. J. Phot. **57**, 781 (1910).
[2] Weinland, J. Opt. Soc. Am. **15**, 341 (1927).
[3] Caroll, J. Phys. Chem. **29**, 693 (1925).
[4] Mauz, Zeits. f. wiss. Phot. **27**, 49 (1929).
[5] Narbutt, Zeits. f. wiss. Phot. **31**, 146 (1932).
[6] Bullock, Sci. et Ind. Phot. (2) **3**, 201, 241 (1932); (2) **4**, 6, 33 (1933).
[7] Jausseran, Sci. et Ind. Phot. **9**, 85, 167 (1929).
[8] Blair and Leighton, J. Phys. Chem. **36**, 1649 (1932).
[9] Blair and Hylan, J. Opt. Soc. Am. **23**, 353 (1933).
[10] Zimmerman, J. Opt. Soc. Am. **23**, 342 (1933).

rate while the reverse reaction is still relatively slow we might expect the density of the latent image to increase for a time. Whether or not such an increase occurs, and to what extent, would depend, as the authors[9] have pointed out in a previous article, upon the type of emulsion, upon the intensity and the wavelength of the illumination used, and upon the particular point of the characteristic density-exposure curve at which the exposure was terminated. Thus it is logical for some investigators to find an increase and others not.

Recently Blair and Leighton[11] have shown that heat has an effect upon the photographic emulsion similar to that of light; that the equation for the rate of formation of the latent image by heat is the same as that which they had developed for its formation by light;[8] and that *temperature* plays a role in certain respects similar to that of *intensity of illumination*. Since heat at ordinary temperatures is much less effective than light in producing the latent image, the storing of exposed emulsions in the dark at these temperatures is somewhat analogous to storing them under faint illumination or long wavelengths. We should expect, then, an effect similar to the *Herschel effect*. From the work of Joehnck and Blair[12] on the Herschel effect we might also expect that in this reversal the latent image would be asymptotically approaching an equilibrium density; that this equilibrium density would depend upon the temperature at which the plates were stored—being higher for higher temperatures, and upon the presence or absence of desensitizers; and that the rate of change of density would vary with the temperature.

## Experimental

In order to test the correctness of these expectations nine plates, following approximately the technique of Narbutt,[5] were exposed for 5 seconds at 80 cm from a 16 cp. carbon filament lamp, cut into pieces approximately 2 cm square, and then treated as indicated in Table I. The plates used were all Agfa Diapositives, hence the experimental results apply only to that particular emulsion, but it is the opinion of the authors that further investigation with other emulsions will yield analogous results.

Table I.

| | Bathed in water | Bathed in pinacryptol yel. | Bathed in pinacryptol yel. & in KBr |
|---|---|---|---|
| Stored at 40°C | *A* | *B* | *C* |
| Stored at 20°C | *D* | *E* | *F* |
| Stored at 0°C | *G* | *H* | *I* |

Immediately after drying, one piece from each plate was developed for 4 minutes at 20°C in elon-hydroquinone developer (Eastman Kodak formula D73 stock diluted 1 : 3), fixed, washed and dried. At various times thereafter, extending over a period of more than six months, other pieces of the plates were removed from storage, developed, fixed and washed.

The densities were measured with a photoelectric cell densitometer of the type previously described by the authors.[13] The curves obtained by plotting the measured densities (ordinates) against hours of storage (abscissae) are shown in Figs. 1, 2 and 3. Although some of the densities measured were for plates which had been stored for over 4800 hours, the change in slope of the curves beyond 360 hours was so gradual as to make that segment nearly a straight line. Hence, in order to show the relative curvatures where they were greatest, only the first 360 hours have been plotted.

Several features of the curves are worthy of comment. The initial densities of the plates *C*, *F* and *I*, which had been treated with both desensitizer and bromide, were only about half

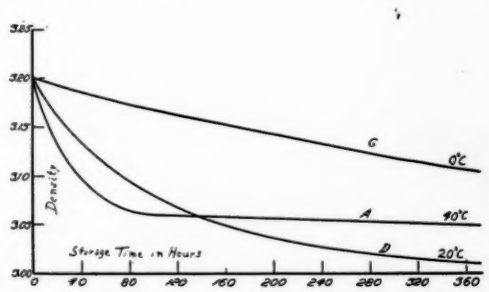


Fig. 1. Bathed in water.

[11] Blair and Leighton, J. Opt. Soc. Am. **24**, 185 (1934).
[12] Joehnck and Blair, J. Opt. Soc. Am. **23**, 67 (1933).
[13] Blair Hylan and Merideth, Phot. J. **409** (Sept. 1933).

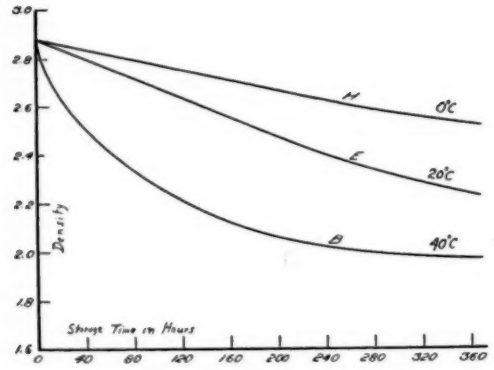


FIG. 2. Bathed in dye.

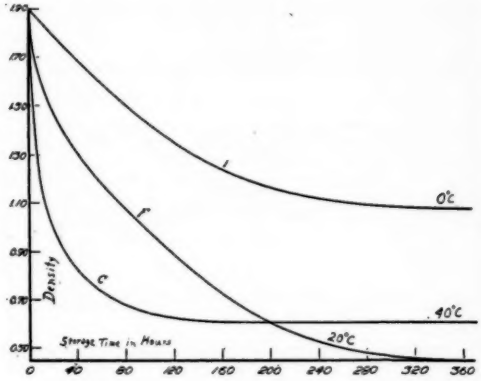


FIG. 3. Bathed in dye and KBr.

those of the untreated plates (*A*, *D* and *G*), while those which had been treated with desensitizer alone (*B*, *E* and *H*), were about nine-tenths of those of the untreated ones. In the three plates (*A*, *D* and *G*) which had been bathed in water before storage, but had been stored at different temperatures, the initial rate of decrease of density was most rapid on the plate which had been stored at the highest temperature, and least rapid on the plate which had been stored at the lowest temperature. The same effect is to be noted in each other set of plates which had received similar pre-storage treatment. This might have been expected from the general effect of temperature on the speed of any chemical reaction. In Figs. 1 and 3 the curves for the plates stored at 20°C, while at first not dropping as rapidly as those for the plates stored at 40°C, after 150 to 200 hours have crossed the latter and are continuing downward. Given sufficient time it is probable that curve *E* (Fig. 2) would similarly cross curve *B*. From our hypotheses and from the work of Joehnck and Blair[12] on the Herschel effect this crossing of curves was to be expected. Furthermore, on the same bases, it is to be expected that curve *G* (Fig. 1), curve *H* (Fig. 2), and curve *I* (Fig. 3) would each, after a sufficiently long period of time, cross the other two curves of its figure and would asymptotically approach the horizontal, so that the initial relative positions of each set of three curves would finally become completely reversed. From a survey of Figs. 1, 2 and 3 it seems probable that such a condition exists.

# The Theory of the Maximum Visual Efficiency of Colored Materials

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The term "visual efficiency" is used here to represent interchangeably the concepts of visual transmission factors of filters and of visual reflection factors of reflecting surfaces. Fluorescent substances are excluded from consideration. A material exhibits hue because visible radiation in some wavelength bands is more or less completely absorbed. This partial absorption of incident energy, necessary for the appearance of hue, obviously decreases the visual efficiency below the unit efficiency characteristic of a nonabsorbing, hueless, white material. Of all the conceivable spectrophotometric curves of materials exhibiting a given chromaticity when illuminated with light of a specified quality, there must be at least one which yields a maximum value for the visual efficiency. This paper describes the general type of spectrophotometric curve which is known to have this unique property. A new proof of the validity and uniqueness of this type of curve is presented. This proof takes advantage of the simplifications made available by the adoption of the I. C. I. 1931 coordinate system for colorimetry.

FROM his experimental survey of the chromaticity range of real pigments, Ostwald[1] drew the empirical conclusion that the attainment of maximum saturation with a pigment required that the spectral reflectance have only the values unity or zero (with discontinuous transitions of the spectrophotometric curve between these values). Furthermore, he concluded that such pigments should have either a single continuous transmission band or a single continuous absorption band in the visible region of the spectrum.

Schrödinger[2] examined the problem of specifying the spectrophotometric characteristics of pigments which should have the maximum attainable reflectance for a given chromaticity (dominant wavelength and purity). His discussion was based on the fundamental properties of the normal human observer as revealed by color mixture experiments. From the convexity of the spectral locus specified by these color mixture data for any coordinate system, and from the additive properties of color mixture diagrams so constructed, he succeeded in establishing a logical confirmation of Ostwald's empirical rule.

Luther,[3] Nyberg[4] and Rösch[5] have computed the loci in the color mixture diagram which bound all chromaticities attainable with pigments having specified visual reflection factors under various illuminants. Independently of these workers, Gage[6] computed the maximum attainable transmission of highly saturated red filters and presented the methods and results before a meeting of the Optical Society of America. All of these computations were made prior to the adoption of the I. C. I. coordinate system for colorimetry.[7]

The conclusions of Ostwald and of Schrödinger can be regarded as corollaries of the following theorem: The maximum attainable purity (closest approach to the corresponding spectral color) for a material having a specified dominant wavelength and visual efficiency will be attained if the material has a spectrophotometric curve which is everywhere either zero or unity, and which has at most two transitions between these values within the region of visible radiation. This theorem is valid for any definition which causes purity to increase continuously during the transition from the neutral toward fully saturated spectral or purple hues. In particular, excitation purity which is defined exclusively by and for a specified coordinate system as the fraction of the distance from the neutral toward the associated saturated hue, spectral or purple, satisfies this condition.

[1] W. Ostwald, Königle Sächs. Ges. d. Wiss. Abh. d. Math.-Phys. **34**, 471 (1917); Physik. Zeits. **17**, 328 (1916).

[2] Erwin Schrödinger, *Theorie der Pigmente von grösster Leuchtkraft*, Ann. d. Physik **62**, 603 (1920).

[3] Luther, Zeits. f. tech. Physik **8**, 540 (1927).

[4] Nyberg, Zeits. f. Physik **52**, 407 (1928).

[5] S. Rösch, Fortshritte der Mineral., Krist. & Petr. **13**, 143 (1929).

[6] H. P. Gage, J. O. S. A. and R. S. I. **18**, 167 (1930).

[7] D. B. Judd, *The I. C. I. Standard Observer and Coordinate System for Colorimetry*, J. Opt. Soc. Am. **23**, 359 (1933).

The proof of this theorem assumes a particularly simple and readily comprehended form if the problem is shown to be equivalent to a certain mechanical problem. The equivalence of the colorimetric problem to this mechanical problem makes it possible to use familiar theorems concerning centers of gravity and moments in order to deal expeditiously with the relatively unfamiliar color problem. The notation used follows that adopted by Judd with a few slight modifications and additions.

$\bar{x}_\lambda$, $\bar{y}_\lambda$, $\bar{z}_\lambda$ are the I. C. I. color mixture functions giving the amounts of three unitary stimuli necessary to produce, in an additive mixture, a visual color match with a unit amount of radiation of wavelength $\lambda$.

$E_\lambda$ is the coefficient of $d\lambda$ giving the power (per unit area) of radiation incident on the sample and having wavelengths in the region from $\lambda$ to $\lambda+d\lambda$.

$r_\lambda$ is the ratio of the power of the radiation of wavelength $\lambda$ reflected or transmitted by the sample to the power of the radiation of the same wavelength incident on the sample.

$X$, $Y$, $Z$ are the amounts of the above-mentioned unitary stimuli necessary to match in color the light reflected or transmitted by the sample.

$$X=\int_0^\infty \bar{x}_\lambda E_\lambda r_\lambda d\lambda,\quad Y=\int_0^\infty \bar{y}_\lambda E_\lambda r_\lambda d\lambda,\quad Z=\int_0^\infty \bar{z}_\lambda E_\lambda r_\lambda d\lambda.$$

$x_\lambda$, $y_\lambda$ are the coordinates in the color mixture diagram of the point representing the chromaticity of radiation of wavelength $\lambda$.

$$x_\lambda=\bar{x}_\lambda/(\bar{x}_\lambda+\bar{y}_\lambda+\bar{z}_\lambda),\quad y_\lambda=\bar{y}_\lambda/(\bar{x}_\lambda+\bar{y}_\lambda+\bar{z}_\lambda).$$

$x$, $y$ are the coordinates in the color mixture diagram of the point representing the chromaticity of the sample when illuminated with light having the energy distribution $E_\lambda$. By analogy with $x_\lambda$, $y_\lambda$ and consistent with the additive properties of vision,

$$x=X/(X+Y+Z),\quad y=Y/(X+Y+Z).$$

From the definitions:

$$(X+Y+Z)=\int_0^\infty(\bar{x}+\bar{y}+\bar{z})_\lambda E_\lambda r_\lambda d\lambda=\int_0^\infty m_\lambda d\lambda.$$

The symbol $m_\lambda=(\bar{x}+\bar{y}+\bar{z})_\lambda E_\lambda r_\lambda$ has been introduced as an abbreviation in this expression. From the expressions for $x_\lambda$, $y_\lambda$ it is evident that

$$\bar{x}_\lambda E_\lambda r_\lambda=x_\lambda m_\lambda,\quad \bar{y}_\lambda E_\lambda r_\lambda=y_\lambda m_\lambda.$$

Consequently.

$$X=\int_0^\infty x_\lambda m_\lambda d\lambda \quad\text{and}\quad Y=\int_0^\infty y_\lambda m_\lambda d\lambda,$$

and

$$x=\int_0^\infty x_\lambda m_\lambda d\lambda/\int_0^\infty m_\lambda d\lambda,$$

$$y=\int_0^\infty y_\lambda m_\lambda d\lambda/\int_0^\infty m_\lambda d\lambda.$$

If $m_\lambda$ is now regarded as a mass per unit wavelength interval along the spectrum locus in the color mixture diagram, $x$, $y$ are evidently the coordinates of the center of gravity of this mass distribution, defined by

$$m_\lambda=(\bar{x}+\bar{y}+\bar{z})_\lambda E_\lambda r_\lambda.$$

For the normal observer and a given illuminant, $m_\lambda$ has a maximum value corresponding to $r_\lambda=1$ and a minimum value, zero. Under the same conditions the visual efficiency is proportional to $Y$ because the visibility function is identical with $\bar{y}$. Consequently visual efficiency, $R$, is proportional to the moment of the mass distribution about the $x$ axis, $R=\text{const.}\int_0^\infty y_\lambda m_\lambda d\lambda$.

Consider a material having the spectrophotometric curve indicated by the full line in Fig. 1a. The point representing the chromaticity of this material is the center of gravity of the spectrum locus weighted in the above manner to the greatest possible extent everywhere between $\lambda_1$ and $\lambda_2$; ($r_\lambda=1$). Let this center of gravity be $C_1$. The dominant wavelength, $\lambda_0$, is the wavelength associated with the point on the spectrum locus collinear with $C_1$ and the white point, see Fig. 2. The white point is the center of gravity of the spectrum locus weighted everywhere to the maximum extent possible for the illuminant considered. The visual efficiency is $R=k\int_0^\infty y_\lambda m_\lambda d\lambda$. The dotted line in Fig. 1 indicates a modification of this spectrophotometric curve of such a character as to maintain $\lambda_0$ and

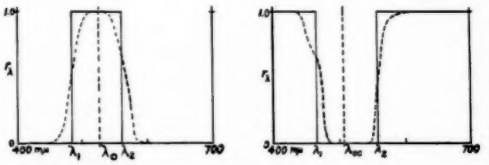


FIG. 1a. Spectrophotometric curves for two green samples having dominant wavelength about 525 mμ and visual efficiency about 0.50. Box shaped curve, full line, has maximum attainable purity.

FIG. 1b. Spectrophotometric curves for two purple samples complementary to 505 mμ and having visual efficiency about 0.50.

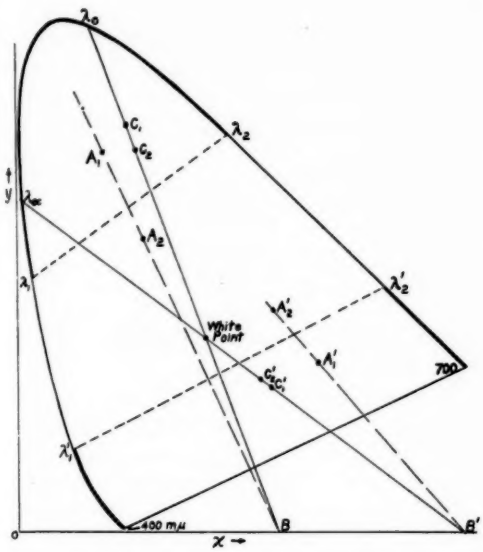


FIG. 2. Color mixture diagram according to I.C.I. standardization, with construction used in proof that box shaped spectrophotometric curve results in maximum purity for every specified dominant wavelength and visual efficiency.

$R$ constant. $C_2$ is the center of gravity of the distribution determined by this altered spectrophotometric data. Subtraction of mass from the original distribution is the only conceivable change that can be made in the region for which $r_\lambda$ was originally unity. Suitable masses must be added outside of the limits of the original distribution in order to keep $R$ unchanged. The amounts of these added masses depend on their distribution and on the amounts and distribution of the subtracted masses. These added masses are determined by the condition that $\lambda_0$ and $R$ remain constant. The center of gravity of the subtracted masses is at $A_1$. The point $A_2$ is the center of gravity of the added masses. All of the subtracted masses, and consequently their center of gravity $A_1$, must lie on the same side of the line connecting $\lambda_1$ and $\lambda_2$ as does $C_1$. Similarly, $A_2$ must lie on the opposite side of this line. The point $B$ is the center of gravity of $A_1$ and $A_2$ weighted, respectively, with $-m_1$ (the total subtracted mass) and $+m_2$ (the total added mass). The point $B$ must lie along the $\lambda_0$ locus because $C_2$, the center of gravity of $C_1$ and $B$, must lie on the $\lambda_0$ locus. The point $B$ must also lie on the $x$ axis because the moment of $m_2-m_1$ about the axis must be zero in order to keep $R$ constant. This same condition requires that $m_2-m_1$ be positive when $A_1$ is farther from the $x$ axis than $A_2$, and negative when $A_2$ is farther from the $x$ axis than $A_1$. It is therefore evident from the diagram that if $C_1$ is farther than the white point from the $x$ axis, $m_2-m_1$ will be positive. Since the total mass has increased, while the moment of this mass about the $x$ axis has remained fixed, $C_2$ must lie closer to the $x$ axis than does $C_1$. Consequently $C_2$ lies closer to the white point than does $C_1$. If $C_1$ is lower than the white point, $m_2-m_1$ will be negative and $C_2$ again will be closer to the white point than $C_1$. In all cases the variation of the spectrophotometric curve from the original (solid curve) results in a decrease in purity for an assigned $\lambda_0$ and $R$. The same argument will evidently apply for the purple material whose spectrophotometric curve is shown in Fig. 1b. Fig. 2 contains the construction necessary for following the above reasoning in this case. The primed letters refer to the purple case. If purity is measured so as to increase continuously as $C_1$ becomes more distant from the white point, along any straight line through the white point, then the terminology for spectral colors will carry over to the discussion of the purples.

The above reasoning has shown that there is a maximum attainable purity corresponding to every specified pair of values of dominant wavelength and visual efficiency. This maximum purity is attained only if the spectrophotometric data of the colored material are either zero or unity at every wavelength in the visible spectrum, with no more than two transitions between these values within the visible range. Of two such samples having the same dominant wavelength, the one exhibiting the higher efficiency invariably exhibits the lower purity. Consequently the fact that there is a maximum attainable efficiency determined by each specified chromaticity can be regarded as a corollary of the maximum purity theorem. The spectrophotometric characteristics necessary to attain this maximum efficiency are identical with those necessary to attain maximum purity. Maximum efficiency and maximum purity can be regarded interchangeably as functions of each other, the

nature of the functions depending on dominant wavelength.

A subsequent paper will present the data for the dependence of maximum visual efficiency on chromaticity. These data will be represented in tabular form with dominant wavelength and excitation purity as chromaticity variables, and also in charts showing the loci of chromaticities characterized by equal maximum efficiencies traced in the I. C. I. color mixture diagram. These tables and charts will be given for I. C. I. illuminants *A* and *C*.

The author wishes to express his appreciation of the interest and assistance of Professor Arthur C. Hardy during the preparation of this paper.

# Disk Colorimetry; Including a Comparison of Methods for Computing Tristimulus Values for Certain Disks

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This report provides a certain amount of information necessary for careful work with the disk method of colorimetry. Color temperatures are given for lamp and filter combinations of available instruments. Tristimulus specifications are given: for several Munsell papers under I. C. I. standard illuminants; for certain glossy papers under diffuse and 45° directional illumination; for colors made in the Munsell laboratory to match other colors when it was necessary to use different pigments; for several methods of computation, by summation for 5 and 10 mμ intervals, and by 10 and 30 selected ordinates; for curves differing slightly from each other; and for color differences significant in cotton grading. These last-mentioned figures are given as a basis for the comparison of the significance of all of the other differences.

FOR use with the disk method of colorimetry, it is necessary for careful work, to have (1) information concerning the color temperature of illumination and (2) careful measurements of the papers used with the instrument.

## 1. Color Temperature of Illuminant

There are, or have been available, three types of instruments[1] for use with the disk method of colorimetry, the first disk colorimeter[2] made by Keuffel and Esser Company in which two 400w, 155v, G30, Mazda clear spotlight, C–5 fil. lamps are used; the second, a revised disk colorimeter[3] made by Keuffel and Esser in which two 250w, 50v, Mazda, C–13, T–10, lamps are used; and third, the Bausch and Lomb HSB color analyzer[4] in which eight 6–8v, Mazda 88–15 C, lamps are used.

Six each of the 400-watt lamps, measured by the writer through the courtesy of the Colorimetry Section of the National Bureau of Standards on their equipment, gave an average of 2900°K at 105 volts, with a range of 2890°K–2925°K. The filters used with these 400-watt lamps consist of 3.6 mm thicknesses of Corning Daylite glass, supplied by Macbeth from the December 21, 1926 melt. From measurements made on this filter at the Bureau of Standards,[5] the approximate color temperature of the lamp and filter combination computed for the lamps operated to give 2900°K is 4520°K; with the lamp at 3000°K, it is 4770°K.

Six each of the 250-watt lamps, measured on Bureau of Standards equipment, gave an average of 2895°K at 40 volts, with a range of 2880°K –2915°K. A daylight filter of 1.7 mm thickness is used with these lamps. From measurements of the filter,[5] the approximate color temperature of the lamp and filter combination, with the lamps operated to give 2900°K is 4260°K; operated to give 3000°K, it is 4480°K.

The color temperature of the 6–8-volt lamps, according to information supplied by Dr. Forsythe in a letter dated November 12, 1934, is 3190°K at 8 volts; 2865°K at 6 volts; and 2675°K at 5 volts. The transformer used in the Bausch and Lomb HSB color analyzer should have an output of 6 volts with an input of 115 volts. The filter used with these lamps is a Corning Daylite glass, 5.5 mm thick. From measurements made of the filter,[5] the color temperature of lamp and filter combination, with the lamp operated at 2700°K is approximately 6350°K; operated at 2800K, the resulting color temperature is 6940°K°.

## 2. Spectral Reflectance Data and Tristimulus Specifications for Selected Munsell Papers

The notation of the Munsell system is useful in color specification. Other papers than the

[1] A fourth instrument, made by the Wallace & Tiernan Company of Newark, N. J., for work especially with wheat flours, has been recently called to the writer's attention. Information regarding the color temperature of its illumination is not at present available.

[2] Pictured in Figs. 14, 15 and 17 of U. S. Dept. Agr. Technical Bulletin 154.

[3] Dorothy Nickerson, J. Opt. Soc. Am. **21**, 640 (1931).

[4] J. W. Forrest, Paper Trade Journal, Nov. 30, 1933.

[5] B. S. Test No. 433z–86/34.

Munsell may be used in disk colorimetry, but the Munsell series provides a wide selection, the papers are carefully painted, they bear the Munsell notation, and may be purchased in convenient form. However, as instruments become available for wider application of this method of colorimetry, it is evident that more information concerning these papers must be made available to others than the very few who already are familiar with the various difficulties and advantages of using them.

Until this entire series of papers is carefully measured for spectral reflectance and is converted into tristimulus specifications, we shall not have an adequate basis for answering disk-mixture questions. In the Munsell laboratory measurements were made several years ago on the Guild instrument and the results transformed to tristimulus specifications in terms of the O. S. A. standard observer. This information has not, however, been published. Dr. Godlove has since been converting these measurements to equivalent I. C. I. data, but the work is not completed. Two papers have been presented to this society based on these data.[6, 7] Meanwhile, measurements of all the Munsell papers have been made in the Color Measurements Laboratory at the Massachusetts Institute of Technology, and the writer understands that work is in progress on the problem of converting these curves into tristimulus specifications.

Pending the time when such information is made available, the disk method, using Munsell papers and notation, has been too useful to lay aside. Various formulas, surrounded by appropriate precautions, have been developed and used for specific purposes.[8, 9] These formulas do not hold when applied without reference to their limitations, yet they serve a useful purpose until such time as information is assembled that will provide accurate tables, charts, or formulas for conversion of disk areas to equally stepped scales of hue, brilliance, and saturation. Tables I–IV give a portion of such necessary information.

The most saturated color of each of the ten principal hues of the Munsell system, plus that of the YR on the 7 brilliance level, have been carefully standardized for work in our laboratories. Tristimulus specifications for these papers under the several I. C. I. standard illuminants have been calculated from spectral reflectance measurements made by the National Bureau of Standards, at 10 m$\mu$ intervals by the use of the I. C. I. data.[10] These specifications, and those for other Munsell papers which have been measured at the Bureau of Standards for our standards work, are included in Table 1. The $y_w$, and $x$ and $y$ values are given, the $z$ values, since they are always 1.0 minus $x+y$, being omitted. Particular attention should be called to the two sets of readings on glossy surface papers, (5R2.6/13 and 2.5R6/12), one set for spectral reflectance data taken under diffuse illumination, the other for directional illumination at 45°. Attention should also be called to the two sets of readings for YR 6/8 and Y 8/9 which demonstrate the closeness with which the Munsell papers can be matched. A special set of these colors had to be made up, after the publication of the new Standard colors had superseded the Atlas colors, and after the supply of pigments formerly used in matching these colors had been exhausted. At the time of painting, it was noted that the colors did not match under all lights, presumably because of a difference in the pigments used. They were matched for a color temperature of about 5700°K.

The color differences which are important in grading work are very small. Therefore, in order to compare the order of difference due to different methods of computation with the order of differences important in grading, a series of tristimulus specifications were made for the same spectral reflectance data by summation for 5[11] and for 10 m$\mu$[10] intervals, and by a

[6] I. H. Godlove, *Standardization of Munsell Colors*, J. Opt. Soc. Am. **22**, 428 (1932).

[7] A. E. O. Munsell, and I. H. Godlove, *Colorimetry with Reflection Standardization*, J. Opt. Soc. Am. **23**, 194 (1933).

[8] Dorothy Nickerson, *Color Tables for Converting Areas of Selected Disks to Terms of Hue, Brilliance, and Chroma.* Mimeographed report, Bur. Agri. Economics, U. S. D. A., 1935.

[9] I. H. Godlove, *Color Blending Computations in Psychological Terms*, J. Opt. Soc. Am. **25, 44**, (1935).

[10] D. B. Judd, *The 1931 I. C. I. Standard Observer and Coordinate System for Colorimetry*, J. Opt. Soc. Am. **23**, 365 (1933).

[11] T. Smith and T. Guild, *The C. I. E. Colorimetric Standards and Their Use*, Trans. Opt. Soc. **33**, 105 (1931–32).

TABLE I. *Tristimulus specifications of selected Munsell colors.* Computations made from N.B.S. spectral reflectance measurements for diffuse illumination[1] and from Judd tables[2], at 10 mμ intervals. Values of *z* are omitted.

| Sample Notation | Spectral reflectance data from N.B.S. Report No. | Date | I.C.I. Illuminant "C"—6500°K 0.3101 0.3163 $y_w$ | $x$ | $y$ | I.C.I. Illuminant "B"—4800°K 0.3485 0.3517 $y_w$ | $x$ | $y$ | I.C.I. Illuminant "A"—2848°K 0.4476 0.4075 $y_w$ | $x$ | $y$ | Equal energy $y_w$ | $x$ | $y$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| R 4/14 | 431 fgh | 10/'34 | 0.1293 | 0.5352 | 0.3106 | 0.1415 | 0.5723 | 0.3226 | 0.1790 | 0.6340 | 0.3309 | 0.1487 | 0.5595 | 0.3164 |
| YR 6/12 | | | .3216 | .5020 | .4110 | .3389 | .5255 | .4136 | .3848 | .5726 | .4042 | .3566 | .5189 | .4099 |
| YR 7/10 | | | .4156 | .4712 | .3980 | .4348 | .5005 | .4064 | .4858 | .5591 | .4049 | .4587 | .4913 | .4003 |
| Y 8/12 | | | .5510 | .4578 | .4754 | .5670 | .4786 | .4727 | .6023 | .5265 | .4522 | .5992 | .4728 | .4713 |
| GY 7/10 | | | .4280 | .3915 | .4920 | .4314 | .4155 | .4961 | .4330 | .4737 | .4846 | .4595 | .4075 | .4931 |
| G 5/8 | | | .1928 | .2566 | .4155 | .1869 | .2824 | .4459 | .1693 | .3569 | .4909 | .2025 | .2726 | .4343 |
| BG 4/6 | | | .1329 | .2283 | .3191 | .1277 | .2547 | .3575 | .1142 | .3400 | .4312 | .1388 | .2444 | .3399 |
| B 4/8 | | | .1153 | .1990 | .2394 | .1091 | .2211 | .2770 | .0946 | .3041 | .3673 | .1190 | .2128 | .2594 |
| PB 3/12 | | | .0817 | .1861 | .1778 | .0764 | .2052 | .2106 | .0653 | .2860 | .3027 | .0835 | .1984 | .1943 |
| P 4/12 | | | .1246 | .2804 | .1800 | .1260 | .3282 | .2164 | .1348 | .4712 | .2972 | .1348 | .3084 | .1974 |
| RP 4/12 | | | .1420 | .3857 | .2416 | .1496 | .4420 | .2732 | .1751 | .5734 | .3260 | .1585 | .4199 | .2575 |
| YR 6/8 (Atlas) | 431a—11 | 5/'28 | .3677 | .4866 | .4069 | .3857 | .5131 | .4113 | | | | | | |
| Y 8/9 (Atlas) | | | .5717 | .4411 | .4604 | .5861 | .4659 | .4610 | | | | | | |
| GY 6/8 (Atlas) | | | .4131 | .3729 | .4650 | | | | | | | | | |
| N 6/ (Atlas) | | | .3750 | .3101 | .3163 | | | | | | | | | |
| #37 N[3] | | | .4329 | .3100 | .3163 | .4329 | .3483 | .3518 | | | | | | |
| #57 N[3] | | | .8535 | .3129 | .3215 | .8538 | .3512 | .3562 | | | | | | |
| 10YR 4/4 | 431a—18 | 3/'30 | .1347 | .4281 | .4038 | | | | | | | | | |
| 10Y 4/4 | | | .1399 | .3810 | .4220 | | | | | | | | | |
| N 4/ | | | .1273 | .3134 | .3193 | | | | | | | | | |
| N 1/ | | | .0170 | .3148 | .3204 | | | | | | | | | |
| 10YR 5/6 | | | .2170 | .4355 | .4083 | | | | | | | | | |
| 10Y 5/5 | | | .2155 | .4011 | .4549 | | | | | | | | | |
| N 5/ | | | .1973 | .3088 | .3163 | | | | | | | | | |
| 5R 2.6/13[4] | 431a—31 | 2/'31 | .0867 | .4903 | .3185 | | | | | | | | | |
| 2.5YR 5/12[4] | | | .2836 | .5080 | .3866 | | | | | | | | | |
| 5R 2.6/13[4] (45° ill.) | 431a—31 | 4/'31 | .0548 | .6217 | .3264 | | | | | | | | | |
| 2.5YR 5/12[4] (45° ill.) | | | .2680 | .5439 | .4034 | | | | | | | | | |
| YR 6/8 (Special)[5] | | | .3683 | .4811 | .4081 | .3856 | .5080 | .4129 | | | | | | |
| Y 8/9 (Special)[5] | | | .5635 | .4417 | .4585 | .5784 | .4660 | .4608 | | | | | | |

[1] Except as otherwise noted.
[2] J. Opt. Soc. Am. **23**, 365 (1933).
[3] These neutrals are a part of a special series. The notations given them by the Munsell Company are N 7.01/ and N 9.40/.
[4] These papers are glossy surface papers made up specially for measuring tomato colors. The *x* and *y* values are given for measuring both under diffuse and 45° illumination. The results are very different, as might be expected.
[5] Papers made specially to match Atlas colors. New pigments used. Matched for approximately 5700°K.

TABLE II. *Tristimulus specifications compiled by different methods from the same spectral reflectance data.*

| Sample notation | Nat. Bur. Standards Spectral Reflectance Data, Report 431 *fgh*—70/34 Computations all made for I.C.I. Illuminant "C" 5 mμ intervals[1] $y_w$ | $x$ | $y$ | 10 mμ intervals[2] $y_w$ | $x$ | $y$ | 30 selected ordinates[3] $y_w$ | $x$ | $y$ | 10 selected ordinates[4] $y_w$ | $x$ | $y$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| R 4/14 | 0.1296 | 0.5351 | 0.3108 | 0.1293 | 0.5352 | 0.3106 | 0.1293 | 0.5352 | 0.3104 | 0.1280 | 0.5367 | 0.3087 |
| YR 6/12 | .3212 | .5019 | .4108 | .3216 | .5020 | .4110 | .3205 | .5027 | .4116 | .3202 | .5041 | .4127 |
| YR 7/10 | .4155 | .4712 | .3978 | .4156 | .4712 | .3980 | .4154 | .4714 | .3984 | .4148 | .4723 | .3992 |
| Y 8/12 | .5501 | .4581 | .4751 | .5510 | .4578 | .4754 | .5503 | .4596 | .4757 | .5499 | .4626 | .4771 |
| GY 7/10 | .4276 | .3919 | .4917 | .4280 | .3915 | .4920 | .4284 | .3933 | .4933 | .4289 | .3959 | .4963 |
| G 5/8 | .1926 | .2564 | .4150 | .1928 | .2566 | .4155 | .1938 | .2562 | .4148 | .1963 | .2529 | .4198 |
| BG 4/6 | .1327 | .2281 | .3184 | .1329 | .2283 | .3191 | .1333 | .2275 | .3195 | .1355 | .2226 | .3239 |
| B 4/8 | .1150 | .1989 | .2390 | .1153 | .1990 | .2394 | .1153 | .1985 | .2400 | .1170 | .1946 | .2427 |
| PB 3/12 | .0815 | .1863 | .1776 | .0817 | .1862 | .1778 | .0821 | .1867 | .1791 | .0808 | .1863 | .1765 |
| P 4/12 | .1242 | .2801 | .1797 | .1246 | .2804 | .1800 | .1226 | .2793 | .1782 | .1195 | .2800 | .1741 |
| RP 4/12 | .1416 | .3858 | .2412 | .1420 | .3857 | .2416 | .1406 | .3857 | .2403 | .1399 | .3866 | .2388 |

[1] These computations were made from the values supplied in Bur. Standards report for the intervals ending in 0, and from values read from curves plotted from those figures for intervals ending in 5. The wavelength scale extended from 380 to 770 mμ.
[2] These computations were made from values supplied in Bur. Standards report, for intervals ending in 10, from 380 to 770 mμ.
[3] These computations were made from values read from curves plotted from data in Bur. Standards report. The curves referred to in [1] were used. The selected ordinates used were those which Professor Hardy was good enough to supply the writer. Readings were made from glass plates on which the ordinates were photographed as guides, the plates being supplied from drawings made in Professor Hardy's laboratory. Checks were made from the wavelength tables where it seemed necessary.
[4] The mid-ordinate of each group of three ordinates read off for the 30 ordinates was used in these computations.

method of selected ordinates, using both 30 and 10 ordinates.[12] The amount of work involved in the latter method might almost be called negligible when compared to that involved in the former, and it is therefore desirable to use if it will give the desired degree of accuracy. Comparisons for eleven selected colors, for summations taken at 5 and 10 mμ intervals, and for 30 and 10 selected ordinates, may be made by reference to Table II. It is evident that data for 100 selected ordinates should also be given, but

[12] A. C. Hardy and O. W. Pineo. *The Computation of Trichromatic Excitation Values by the Selected Ordinate Method*, J. Opt. Soc. Am. **22**, 430 (1932).

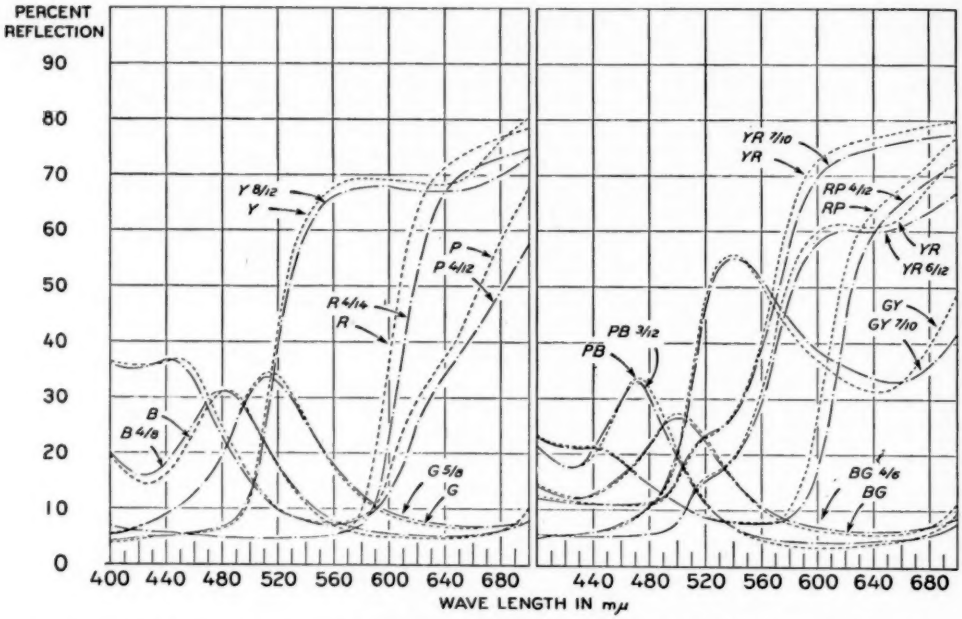


FIG. 1. Spectral reflectance curves of selected colors.—Eleven Munsell colors from N.B.S. Report No. 431 *fgh* —70/34. . . . Curves of slightly different colors, used as a basis for comparison for tristimulus values.

the reading off of a total of 300 points from each plotted curve involves enough chance of differences due to reading from the curve, as against differences due to computation, that it was not attempted. It is understood that the new Hardy recording color analyzer, when equipped with a mechanical integrating device,[13] will make use of 100 selected ordinates.[14] It should be remembered that the number of ordinates used in either method can be selected to give the desired degree of accuracy, although in this connection it should be pointed out that in dealing with colors for which the shape of the spectral reflectance curves is similar, calculations on the basis of a small number of ordinates will indicate the nature of the color differences, even though a large number of ordinates might be necessary to give the correct absolute values.

[13] A. C. Hardy, J. Opt. Soc. Am. **18**, 96 (1929).

[14] Reference should also be made to the Hilger Color Integrator which, as described by Pineo for Hilger, will give the values of nine integrals corresponding to the three international standard illuminants by one tracing of a curve. This integrator does not operate on the selected ordinate method.

In order to compare the order of color difference between spectral reflectance curves that are not too different, a series of hypothetical curves are used as a basis for comparison. These curves are marked, in Fig. 1, only with hue, since their Munsell specification is unknown. Tristimulus specifications for these curves are given in Table III. They should be compared to data for the solid line curves which is given in Table I, under Illuminant "C," the first eleven colors. Color differences shown by tristimulus specifications between curves exhibiting such differences are, in some cases, no more different than differences resulting from several methods of computing a single set of data.

The differences that are important for color measurements on cotton are, as calculated from disk measurement, about 0.50 for hue, 0.10 for brilliance (a maximum, since 0.02 can be recognized in instrumental work), and 0.15 for chroma. In order to compare differences of this order with the data given in Tables I to III, average tristimulus specifications have been calculated for disk areas which match colors exhibiting such differences as these. For example,

TABLE III. *Tristimulus specifications for spectral reflectance of dotted curves in Fig. 1[1] for I.C.I. Illuminant" C," at 10 mμ intervals.*

| Hue notation | $y_w$ | $x$ | $y$ |
|---|---|---|---|
| R | 0.1572 | 0.5517 | 0.3184 |
| YR | .3367 | .5025 | .4137 |
| YR | .4358 | .4736 | .4003 |
| Y | .5668 | .4578 | .4779 |
| GY | .4215 | .3881 | .4962 |
| G | .2013 | .2499 | .4221 |
| BG | .1332 | .2244 | .3227 |
| B | .1081 | .1981 | .2429 |
| PB | .0813 | .1822 | .1790 |
| P | .1351 | .2912 | .1840 |
| RP | .1638 | .4101 | .2518 |

[1] These specifications are given for comparison to those for the solid line curves, given in the first 11 items of Table I.

TABLE IV. *Tristimulus specifications for differences significant in color measurements of cotton made on a basis of disk mixtures.*

The $x$, $y$, $z$ calculations were made by the addition of the $x_w$, $y_w$ and $z_w$ values for the percentages of the disks exposed in making the color match. Calculations are for Illuminant "B" since it is nearest to the illuminant for the instrument on which the measurements were made.

| Sample No. | Disk percentages | | | | Munsell notations | | | Tristimulus specifications | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | YR | Y | N 9.4/ | N 7/ | Hue | Brilliance | Chroma | $y_w$ | $x$ | $y$ |
| 1 | 10 | 10 | 41 | 39 | 1.00Y | 8.08 | 1.70 | 0.6161 | 0.3680 | 0.3659 |
| 2 | 8 | 10 | 40 | 42 | 1.52Y | 8.08 | 1.54 | .6128 | .3662 | .3653 |
| 3 | 8 | 8 | 41 | 43 | 1.00Y | 8.08 | 1.36 | .6140 | .3644 | .3636 |
| 4 | 8 | 10 | 21 | 61 | 1.52Y | 7.60 | 1.54 | .5328 | .3681 | .3659 |
| 5 | 8 | 8 | 14 | 70 | 1.00Y | 7.39 | 1.36 | .5003 | .3667 | .3642 |
| 6 | 13 | 11 | 69 | 7 | 0.59Y | 8.73 | 2.03 | .7341 | .3689 | .3667 |
| 7 | 15 | 12 | 68 | 7 | 0.46Y | 8.70 | 2.28 | .7391 | .3711 | .3678 |
| 8 | 11 | 10 | 65 | 14 | 0.77Y | 8.64 | 1.78 | .7166 | .3669 | .3655 |
| 9 | 12 | 12 | 65 | 11 | 1.00Y | 8.65 | 2.04 | .7199 | .3692 | .3672 |
| 10 | 9 | 9 | 51 | 31 | 1.00Y | 8.32 | 1.53 | .6571 | .3654 | .3645 |
| 11 | 11 | 11 | 51 | 27 | 1.00Y | 8.32 | 1.87 | .6592 | .3688 | .3667 |

YR 6/8 and Y 8/9 of the old Atlas papers, with Special Neutrals No. 57 and No. 37, are mixed in different proportions to match cotton samples, all of which are close in hue and chroma, but not necessarily close in brilliance. The data are given in Table IV. The first three examples are of color differences that are significant for grading work when brilliance does not vary. Between examples 2 and 4, and between 3 and 5, the brilliance differences are large, but those for hue and chroma are the same in Munsell notation. Examples 6 and 7 are extremes of color within a single grade of cotton, differences that are recognized and can be matched in classing cotton. Examples 8 and 9, and 10 and 11, are extremes for two additional grades. The examples have been selected within each grade for constant brilliance, the major differences thus being in hue and chroma which should show up in the tristimulus data. The $y_w$ values are related to the brilliance figures. They would bear the relation given for Munsell brilliance-to-reflectance if the original notations of the disks were accurately given for the illumination used.

From the data of Table IV it may be seen that chromaticity differences which are important in disk colorimetry correspond to $x$ and $y$ differences of about 0.002. It is evident, therefore, that a method of computation is required which gives $x$ and $y$ with an uncertainty no greater than 0.001. The data of Table II indicate that summation for intervals of 10 mμ gives $x$ and $y$ with an average uncertainty of 0.0004, that the 30 selected-ordinate method has an average uncertainty of 0.0010, and that the 10 selected-ordinate method has an average uncertainty for samples such as these of 0.0035. This latter method, therefore, is not sufficiently precise to bring out chromaticity differences which can easily be detected by disk colorimetry, but the former two methods are probably of adequate precision. The less convenient ten-millimicron-summation method is apparently somewhat more precise than the 30 selected-ordinate method but some of the indicated superiority may be spurious because the five-millimicron-summation method taken as correct included the sums found by 10 mμ summation.